

Doped Spin Ladder: Zhang-Rice Singlets or Rung-centred Holes?

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Abstract

We formulate charge transfer model for a single doped spin ladder, relevant for the intrinsically doped plane of coupled spin ladders in $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$. Assuming the presence of the experimentally observed charge order in the system we solve the model using Hartree-Fock approximation. Our results show the profound stability of the Zhang-Rice singlets with respect to other configurations of doped holes, in agreement with recent x-ray absorption measurements.

1 INTRODUCTION

It is a widely accepted feature of two-dimensional high temperature superconducting cuprates (HTSC) [1] that a hole doped into CuO_2 plane enters into a square of O ($2p$) orbitals and strongly binds with the central Cu ($3d$) hole forming a local, so-called Zhang-Rice [2] singlet (ZR; cf. Fig. 1). On the other hand, a hole doped into the HTSC Cu_2O_3 coupled spin ladders can *a priori* behave differently. This is due to the fact that: (i) spin ladders do not have the D_{4h} symmetry (the four O surrounding Cu are not identical), and (ii) for *coupled* spin ladders the coordination number of the leg orbitals ($= 3$) is different than that of the bridge orbital ($= 2$) resulting in lower on-site energy for the hole in the bridge orbital than in one of the leg orbitals, cf. local-density approximation studies in [3]. Hence, one could expect that e.g. a rung-centred state (rung) could be stabilized with a doped hole residing on the O ($2p$) bridge orbital and bound to the two neighbouring Cu holes via kinetic exchange interactions (cf. Fig. 1).

The aim of the present paper is to study the possible stability of *these* two states in the doped spin ladder by means of model calculations. It is an interesting theoretical task by itself, still backed by the recent x-ray absorption measurements which suggest that in the spin ladder plane of $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$ (SCCO) a hole crystal with period $\lambda = 3$ has been discovered with the doped holes evenly distributed among the O $2p$ orbitals involved in the ZR singlet [4]. This stays in contrast with the other experiments which suggest that the holes are not isotropically distributed. E.g. Nücker et al. [5] also in the x-ray absorption measurements find that the doped holes go mainly into those leg orbitals which are responsible for transport properties of the single ladder (crystallographic c direction). Such result, however, not only contradicts those obtained in Ref. [4] but also a naive picture of rather localized holes in this *insulating* compound. Thus, the issue of the distribution of holes doped into spin ladders indeed needs some further studies.

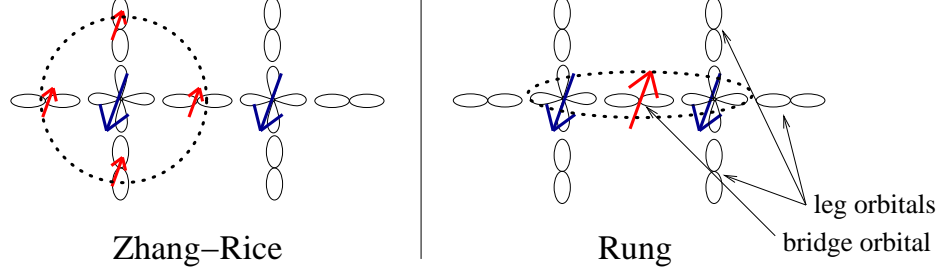


Figure 1: Schematic picture of the Zhang-Rice (ZR) singlet (left panel) and rung-centred (rung) hole (right panel) in a Cu_2O_7 cluster. Large (small) arrows depict the hole spins for +1.0 (+0.25) charge. The grey arrows stand for spins of doped holes.

2 MODEL HAMILTONIAN AND HARTREE-FOCK APPROXIMATION

Our starting point is the three band charge transfer Hamiltonian relevant for a single doped spin ladder [6]:

$$\begin{aligned}
 H = & \left(- \sum_{m,j \in R,L,\sigma} t_{mj} d_{m\sigma}^\dagger p_{j\sigma} - \sum_{m \in R,L;i\sigma} t_{mi} d_{m\sigma}^\dagger b_{i\sigma} + \text{h.c.} \right) + \Delta \sum_{j \in R,L} n_{pj} + \varepsilon \sum_i n_{bi} \\
 & + U \sum_{m \in R,L} n_{m\uparrow} n_{m\downarrow} + U_p \left(\sum_i n_{bi\uparrow} n_{bi\downarrow} + \sum_{j \in R,L} n_{pj\uparrow} n_{pj\downarrow} \right), \quad (1)
 \end{aligned}$$

where: Δ is the charge transfer energy for the O ($2p_\sigma \equiv p$) *leg* orbital, ε is the charge transfer for the O ($2p_\sigma \equiv b$) *bridge* orbital (cf. Fig. 1), t_{mj} is the hopping integral between the nearest neighbour pairs of the Cu ($3d_{x^2-y^2} \equiv d$) orbital and p or b orbitals. We also include Coulomb on-site repulsion U (U_p) between holes in the d (p or b) orbitals, respectively. Besides, the d and p orbitals belong to two sets of sites for the Left ($d_L, p_L \in L$) and Right ($d_R, p_R \in R$) leg of the ladder, and n_m , n_{pj} , n_{bi} are particle number operators for d , p , b orbitals, respectively.

In the following study we assume that the charge order is present in the ladder, as one of the few features of the ladder subsystem of SCCO compound on which the experimentalists agree is the formation of the hole crystal [4]. Therefore we expect that for commensurate values of doping a doped hole forms a ZR or rung bound states which then form a hole crystal of relevant period.

The presence of the charge order enables us to safely use Hartree-Fock approximation which works well for ordered states. This, however, means that we must adopt a classical picture for ZR and rung states: a hole with the opposite S^z component of the spin with respect to the spin of the relevant Cu holes involved in kinetic exchange interactions (with no energy gain due to quantum fluctuations or phase coherence in ZR state).

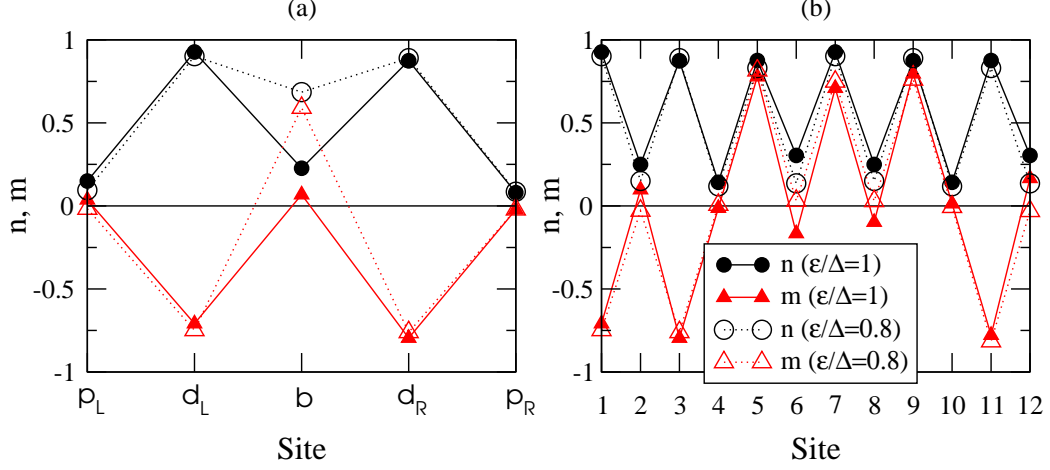


Figure 2: Hole density (n) and magnetization (m) for: (a) sites along the rung with enhanced hole density; (b) 12 consecutive sites along one of the legs of the ladder (starting from the d orbital, ie. for $d-p-d-\dots$ chain). The legend applies to both of the panels.

3 RESULTS AND DISCUSSION

We performed self-consistent numerical calculations using 60×7 (the unit cell of the spin ladder consists of 7 orbitals [6]) clusters for the following model parameters: $U = 9$ eV, $U_p = 4.2$ eV, $\Delta = 3.5$ eV [7], whereas $t = 1$ eV yields the correct superexchange constant $J/t \sim 0.1$, cf. Ref. [8]. We assume that the total number of holes per Cu $n_h = 1.33$ in order to make our results comparable with the recent x-ray absorption measurements in SCCO [4]. Though, let us stress that the stability of ZR or rung states does not depend on the value of the commensurate doping since similar results as shown below were obtained for other values of hole doping [6].

The results for two different values of the bridge orbital energy ϵ are shown in Fig. 2. For $\epsilon/\Delta = 1$ the hole distribution and magnetization resembles the classical ZR state: the doped hole is distributed rather isotropically among four O sites (e.g. sites b and p_L on Fig. 2(a) and sites 2 and 12 on Fig. 2(b)) surrounding the central Cu site occupied by roughly one hole (e.g. site 1 on Fig. 2(b) or d_L on Fig. 2(a)). Also the spin of the doped hole in the O ($2p$) orbitals compensates roughly the spin of the hole in the Cu site. On the other hand, for $\epsilon/\Delta = 0.8$ the doped hole enters mainly into the b orbital and there are much less holes in the p orbitals of the leg of the ladder suggesting a rung character of the doped hole. Let us also note that, in agreement with the assumption of charge order, we find a hole crystal with less charge per every third rung of the ladder for the solution with ZR or rung character.

In order to investigate the role of the specific spin ladder geometry on the stability of ZR and rung states we calculate the densities and magnetization of holes involved in forming: (i) ZR state: $n_{ZR} = n_{p_L} + n_2 + n_{12}$ and $|m_{ZR}| = |n_{ZR\uparrow} - n_{ZR\downarrow}|$ (we exclude the b orbital from the sum to be able to distinguish between rung and ZR states), and (ii) rung state: $n_{rung} = n_b$ and $|m_{rung}| = |n_{rung\uparrow} - n_{rung\downarrow}|$. The results are shown in

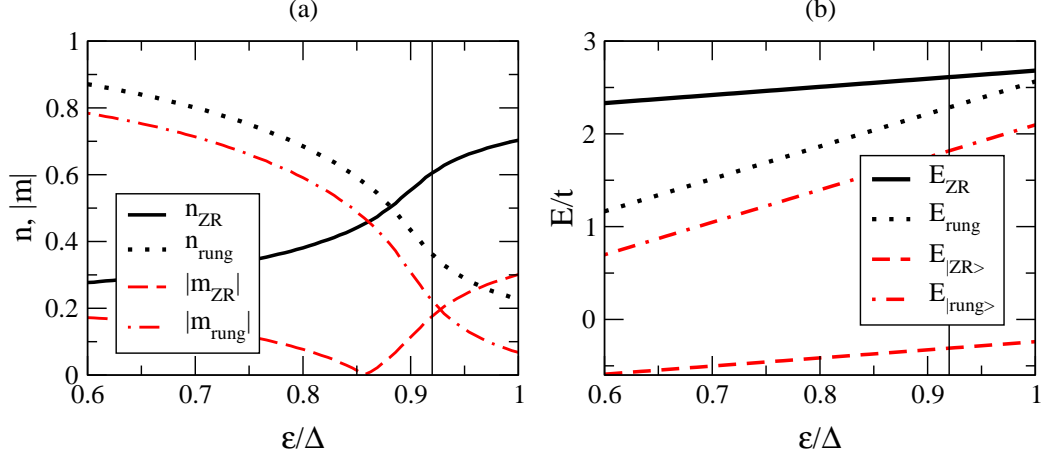


Figure 3: (a) Hole density (n) and absolute value of magnetization ($|m|$) for holes involved in forming ZR (n_{ZR} , $|m_{ZR}|$) and rung states (n_{rung} , $|m_{rung}|$) as a function of the bridge orbital energy ε . (b) Binding energies of a single hole in ZR and rung states in the classical case (E_{ZR} and E_{rung} , respectively) and quantum-mechanical case ($E_{|ZR>}$ and $E_{|rung>}$, respectively) as a function of the bridge orbital energy ε . The vertical line on both panels depicts the value of $\varepsilon/\Delta = 0.92$, cf. Ref. [3].

Fig. 3(a) as a function of the on-site energy of the bridge orbital ε . We find that with the decreasing value of ε doped holes tend to occupy the b orbital, and the spins of the holes in the b orbital become polarized. Besides, the spins of the holes involved in forming ZR state do not only compensate the spin of the central Cu hole but for $\varepsilon/\Delta < 0.85$ even weakly align ferromagnetically with the Cu spin. Hence, we suggest that for $\varepsilon/\Delta < 0.85$ the doped holes show a rung character while for $\varepsilon/\Delta > 0.9$ they show a distinctive ZR character separated by a crossover regime. It means that ZR state is stable for the value of $\varepsilon/\Delta = 0.92$, calculated in Ref. [3], though we are very close to the crossover regime.

Let us now pose the question to what extent our results are relevant for the stability of the real quantum-mechanical Zhang-Rice singlets or rung states. Therefore, using *second* order perturbation theory in U and $U - \Delta$ [9] we calculate the binding energy of a single hole doped into ZR and rung states: in the classical case (E_{ZR} and E_{rung} , respectively), and in the quantum-mechanical case ($E_{|ZR>}$ and $E_{|rung>}$, respectively). In the classical case, which resembles the states obtained in the Hartree-Fock approximation, we have:

$$E_{ZR} = \frac{3}{4}\Delta + \frac{1}{4}\varepsilon + J \left\langle \sum_{i \in ZR} \mathbf{S}_i \cdot \mathbf{S}_O - \frac{1}{4} \right\rangle_{ZR}, \quad E_{rung} = \varepsilon + J \left\langle \sum_{i \in rung} \mathbf{S}_i \cdot \mathbf{S}_O - \frac{1}{4} \right\rangle_{rung} \quad (2)$$

where: the kinetic exchange $J = 2t^2(1/U + 1/(U - \Delta))$, \mathbf{S}_O is the spin of the doped O ($2p$) hole, \mathbf{S}_i is the spin of the Cu ($3d$) hole, and the sum goes over those Cu sites which are involved in forming a bound state with the O ($2p$) hole in rung or ZR state. The expressions for the energies in the quantum-mechanical case look similar except for the averages of the spin operators which, unlike in the classical case, include also spin fluctuations. In addition, for the real ZR singlet we include the phase coherence of holes

doped into the O ($2p$) orbitals [2]. The results as a function of the energy of the bridge orbital ε are shown in Fig. 3(b).

We find for the classical state that for $\varepsilon/\Delta < 0.97$ the energy difference ($E_{ZR} - E_{rung}$) is larger than the effective hopping energy of the O ($2p$) hole ($= t^2/U$ or $t^2/(U-\Delta)$). Hence for finite bandwidth the rung state could only be stabilized up to the above value of the bridge orbital energy, qualitatively in agreement with the previous Hartree-Fock results. However, in the quantum mechanical case the rung state could never be stabilized, and due to the large energy difference ($E_{|ZR\rangle} - E_{|rung\rangle}$) the true Zhang-Rice singlet should not be destabilized by finite bandwidth.

4 CONCLUDING REMARKS

In summary, we have shown the profound stability of the Zhang-Rice singlets in the hole doped spin ladders. First, using model Hartree-Fock calculations we obtain the isotropic distribution of doped holes among the O ($2p$) orbitals surrounding the central Cu ($3d$) hole to be stable for the relevant range of the model parameters. Second, quantum-mechanical calculations of the binding energy of holes forming Zhang-Rice singlets and rung states suggest the Zhang-Rice singlets to be even more stable. Hence, our results provide an interpretation of recent experimental data obtained in the x-ray absorption measurements in the spin ladder plane of SCCO [4].

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